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CATHODE CATALYSTS FOR PRIMARY PHOSPHORIC ACID FUEL CELLS

FINAL REPORT

FRASER WALSH, PROGRAM MANAGER
ECO, DIVISION OF KOR, INC.

DECEMBER, 1981

PREPARED FOR
NATIONAL AERONAUTICS AND SPACE ADMINISTRATION
LEWIS RESEARCH CENTER
UNDER CONTRACT DEN 3-150

FOR
U.S. DEPARTMENT OF ENERGY
ENERGY TECHNOLOGY
DIVISION OF FOSSIL FUEL UTILIZATION

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WASHINGTON, DC 20545
UNDER INTERAGENCY AGREEMENT DE-AI-01-80ET17088

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1.0 EXECUTIVE SUMMARY

This program had two major objectives. One was to improve competitiveness of the phosphoric acid fuel cell in the market place by evaluating additional carbon-bonded metallated dehydrodibenzo tetraazannulene (TAA) derivatives as possible replacements for platinum in cell cathodes. The second was to evaluate whether the perception that commercial polytetrafluoroethylene (PTFE) hydrophobic structural resins, which are used extensively to control wetting in fuel cells, are truly stable during the lifetime (40,000 h) goal of a fuel cell. Under the program, a link tying TAA to a support carbon was identified that was more stable than heretofore known and the metallated TAA-carbon catalyst was shown to be more active, though less stable, than platinum in similarly prepared cathodes at 100°C. PTFE surfaces were shown to be unstable in the fuel cell environment with degradation occurring in 2000 hours or less. Details of some of the key results and achievements are presented below.

Unbonded cobalt TAA, when used as a catalyst in a phosphoric acid fuel cell, was shown to retain 70% of its activity after ten months at 100°C.

After a 100 h break-in period in similarly prepared cathodes at 650 mV, a sample catalyst of cobalt TAA covalently bonded to carbon was compared to platinized platinum at 10 mA/cm² in 100°C 85% phosphoric acid. The TAA product was more active catalytically as shown by its higher cathode potential, 740 mV vs 640 mV_{DHE}, and its lower Tafel slope, 60 mV vs 130 mV per decade. (Bonded cobalt TAA had previously been shown to be more stable than unbonded.)

A dimeric, 3-dimensional variant of the nearly planar cobalt TAA molecule was prepared and bonded to carbon. Pulse voltammetry tests showed the dimeric form to be more active. In addition, it was more stable; the rate of deactivation at 125°C was about equal to the rate of the bonded monomeric form at 100°C. Additional improvements in stability and activity of metallated TAA-carbon catalysts through research is expected.

PTFE was stressed at 200°C in concentrated phosphoric acid as well as electrochemically stressed in 150°C concentrated phosphoric acid; the surface chemistry of PTFE was observed to change significantly as measured by goniometry and by an ESCA technique. Radiolabeled PTFE was prepared and used to verify that such chemical changes also occur in the primary fuel cell environment.

All three analytical methods showed appreciable degradation of the PTFE surfaces in 2000 h applications. An improved resin or changes in cell construction to minimize surface degradation is desirable.

2.0 Objectives and Results Summary

2.1 Objectives

The two major objectives of the program were to evaluate the stability and the electrocatalytic activity of cobalt dihydrodibenzo tetraazannulene (CoTAA) as a function of the ligand used to covalently link the CoTAA to the carbon support surface and to evaluate the stability of polytetrafluoroethylene (PTFE) when used in a primary fuel cell. Another primary objective was to evaluate the chemical stability and the electrocatalytic activity of CoTAA which is heat sintered on the carbon surface and which is also held via two-carbon links so that all planar CoTAA molecules are 'face-to-face'. Tasks were carried out to obtain the data required to meet the following eleven objectives:

1. Functionalize the surface of Vulcan XC-72 (the support carbon) via three types of chemical reactions (acylation, cycloaddition, alkylation) to provide ligand halides covalently linked to the carbon surface;
2. Quaternize the ligands with a ^{14}C -labeled amine and monitor the rate of ^{14}C release to determine the most stable ligand type;
3. Prepare carbon with varying link lengths of the most stable ligand type and react it with bis-aminated TAA;
4. Metallate the bonded-TAA and rank the electrocatalytic activity of the bonded catalyst as a function of link length;
5. Test the stability of the most active bonded catalysts in primary fuel cells;
6. Prepare ^{14}C -labeled polytetrafluoroethylene;
7. Evaluate commercially-available polytetrafluoroethylene after chemical and electrochemical stressing;
8. Test the stability of polytetrafluoroethylene as the wet-proofing agent in cathodes for primary fuel cells using the ^{14}C -labeled material;
9. Prepare metallated butene TAA and heat-sinter it with the carbon support to form a catalyzed carbon with the metallated TAA molecules held 'face-to-face' (dimeric TAA);

10. Test dimeric TAA in primary fuel cells to demonstrate electrochemical activity and chemical stability;
11. Evaluate cathode fabrication procedures to determine effect on catalyst performance.

2.2 Summary of Work

Three different carbon surface functionalization procedures were carried out on Vulcan XC-72. The resulting functionalized carbons were reacted with ^{14}C -labeled trimethyl amine and with ^{14}C -labeled dimethylamino TAA. The release of ^{14}C from these bonded carbons was measured; based on the results obtained, the alkylation procedure of carbon functionalization was identified as providing the most stable bond between the carbon surface and the organic electrocatalyst. This result was confirmed based on evaluation of the electrochemical activity of the bonded catalyst after acid treatment for 31 days.

Following identification of the alkylation functionalization procedure as providing the most stable carbon-ligand bond, the effect of carbon link length in the ligand between the Vulcan XC-72 surface and the organic electrocatalyst was examined. Vulcan XC-72 with four different link lengths was prepared (3, 4, 5 and 6 carbon atoms in the chain), reacted with bis-aminated TAA, metallated with cobalt, and evaluated for electrochemical activity using pulsed voltammetry and as the catalyst in primary fuel cell cathodes. The results of these tests did not show any significant differences in electrochemical activity as a function of number of carbon atoms in the chain. In the half-cell tests, the CoTAA-catalyzed cathodes showed significantly improved performance after 100 hours in 100°C 85% phosphoric acid compared to 10% platinum catalyzed cathodes based both on Tafel slope (factor of two decrease in mV/decade) and on the absolute magnitude of the cathode potential at 10 mA/cm² using 99.95% oxygen as a fuel (740 vs 640 mV). When air was used as a fuel, the platinum catalyzed cathodes suffered a significant performance loss (100 mV at 2.5 mA/cm²) while the CoTAA catalyzed cathodes suffered smaller losses (40 mV at 2.5 mA/cm²).

The stability of polytetrafluoroethylene (PTFE) was examined through two types of experiments. First, commercial samples of PTFE were obtained, formed into test disks, and then stressed chemically and electro-chemically. Significant changes in PTFE surface properties (10° in wetting angle) were observed over 4270 hours when stressed in 200°C 85% phosphoric acid. A similar change in surface property was observed in only 2140 hours when the PTFE was stressed in 150°C 85% phosphoric acid and held on a vitreous carbon disk which was maintained at + 200 mV vs DHE. These changes in surface properties were verified using an ESCA technique to show changes in surface chemistry.

The second PTFE experiment required a complete synthesis of ^{14}C -labeled PTFE from ^{14}C -labeled carbon tetrachloride. The ^{14}C -PTFE was incorporated into platinum-catalyzed cathodes and stressed at 125°C in 85% phosphoric acid using oxygen as the fuel; the cathodes were maintained at + 650 mV vs DHE. Aliquots of the electrolyte were taken over a 4600 hour period and evaluated for ^{14}C -activity; none was observed throughout the test period. At the end of the test, samples of the cathodes were evaluated and an average decrease of 10% in ^{14}C -activity was observed. These two experiments show that the chemical properties of PTFE are changed in the environment of a primary fuel cell cathode.

A second type of TAA catalyst was evaluated: this catalyst was prepared in a manner such that the TAA molecules were held, via covalent carbon links, in parallel planes. Metallated bis-benzocyclobutene TAA was prepared, mixed in a 1:2 ratio with Vulcan XC-72, and heat-sintered at 700°C under nitrogen; the resultant dimeric material was evaluated for electrochemical activity both by pulsed voltammetry and in a primary fuel cell. The data obtained shows the dimeric material to have electrochemical activity equal to 10% platinum on carbon; in long-term fuel cell tests, the dimeric material had an increased temperature stability compared to bonded CoTAA.

The long-term stability of CoTAA-catalyzed cathodes was evaluated during the program. During test periods of 1000 hours in over 100°C 85% phosphoric acid, performance of cathodes catalyzed with CoTAA was observed to decay by approximately 20%. These cathodes were prepared using a simple method of cathode preparation; toward the end of the program, methods involving floccing and improved dispersion techniques were tried: they provided cathodes of improved performance.

3.0 Chemical Preparation Techniques

3.1 Preparation of Bonded CoTAA

3.1.1 Synthesis of Bis-N-dimethyl-aminomethyl TAA

Dihydrodibenzo tetraazaannulene (TAA; Product A) was prepared by reaction of one molar equivalent of o-phenylenediamine in five weight volumes of 1:1 :: ethanol:methanol with one molar equivalent of freshly prepared propargyl aldehyde. The product obtained was purified by recrystallization in cyclohexanone followed by sublimation under vacuum (0.5 mm at 200°C). The purified TAA was reacted with 2.1 molar equivalents of dimethylamine hydrochloride (C_2H_7NHCl ; MW 82) and 2.1 molar equivalents of paraformaldehyde in 20 weight volume equivalents of dioxane. The reaction mixture was held at reflux for 30 minutes, the solvent removed under vacuum, and the residue redissolved in methanol. The methanolic solution was made basic with triethylamine; following removal of excess triethylamine under vacuum, the resulting solution was passed through an aluminum oxide column (Woelm basic grade 1) under a head of nitrogen. The material obtained after removal of the methanol was characterized by IR and mass spectrum to be the desired product: bis-N,N-dimethyl-aminomethyl TAA (Product B, Figure 3.1).

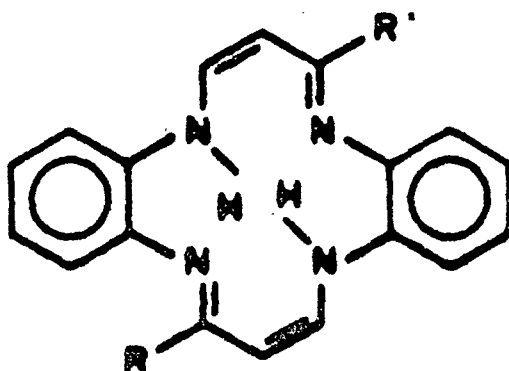
3.1.2 Preparation of Acylated Carbon

23 g of acylated carbon (Product C) were prepared using the following procedure: 24 g of Vulcan XC-72 were reacted with 24 g of 6-bromohexanoyl chloride ($C_6H_{11}ClBrO$; MW 213.5) with 4.8 g of ferric bromide ($FeBr_3$; MW 296). This mixture was held at reflux (101°C) for two days under nitrogen in a 1000 ml 3-neck round-bottom flask. The acylated carbon was harvested by centrifugation and then washed (with centrifugation) successively with nitromethane, methanol, water, methanol and acetone. The acylated carbon was dried under vacuum. After drying, the acylated carbon was soxhletted for six days in methanol, then air dried and finally vacuum dried. Elemental analysis showed this acylated carbon to contain 0.18 mM bromine/g.

3.1.3 Preparation of Cyclized Carbon

9.5 g of the cycloaddition form of functionalized carbon (Product D) were prepared as follows: 10 g of Vulcan XC-72 were heated under vacuum for five hours at 1000°C and then allowed to cool to 100°C. 6 g of 5-chloro-1-pentyne (C_5H_7Cl ; MW 102) were heated to 140°C and then drawn through the heated carbon by vacuum over two hours. The carbon was then collected and soxhletted with toluene for seven days. The carbon was dried under vacuum. Elemental analysis showed this cyclized carbon to contain 0.03 mM chlorine/g.

Figure 3.1 TAA and Aminated TAA



R = H TAA (Product A)

R = CH₂N(CH₃)₂ Aminated TAA (Product B)

3.1.4 Preparation of Alkylated Carbon

Two procedures were followed. 24.8 g of alkylated carbon (Product E) were obtained using the following procedure: 24 g of Vulcan XC-72 were reacted with 24 g of 1-chloro-6-iodohexane ($C_6H_{12}ClI$; MW 246) and 2.2 g of anhydrous aluminum trichloride ($AlCl_3$; MW 133) in 240 ml of freshly distilled nitromethane. The reaction mixture was kept at reflux ($101^\circ C$) for three days under a nitrogen atmosphere in a 2 liter 3-neck round-bottom flask with continuous stirring. The carbon was then collected by centrifugation and washed (with centrifugation) successively with nitromethane, methanol, water, methanol and acetone. The alkylated carbon was soxhletted in methanol for six days and then dried under vacuum. Elemental analysis showed this alkylated carbon to contain 0.08 mM chlorine/g.

9.3 g of alkylated carbon were also obtained by a second procedure (Product F): 12.4 g of Vulcan XC-72 were added to a 500 ml 3-neck flask containing 8.8 g of potassium and 0.608 g of naphthalene ($C_{10}H_8$; MW 128) in 240 ml of freshly distilled tetrahydrofuran (THF) which had been stirred overnight under argon at room temperature. The carbon was allowed to react for 72 hours; the carbon suspension was then cooled to $0^\circ C$ and 21.0 g of 1-chloro-6-iodohexane (in 60 ml of THF) were added dropwise over one hour. The reaction mixture was warmed to room temperature and allowed to stir for three hours. The alkylated carbon was harvested by centrifugation and washed (with centrifugation) successively with ethanol, water, 85% phosphoric acid, water, methanol and toluene. The alkylated carbon was soxhletted in toluene for six days and then dried under vacuum. Elemental analysis showed this alkylated carbon to contain 0.12 mM chlorine/g.

In studying the effect of the number of carbons in the link between the carbon and the TAA on electrochemical performance, three other alkylated carbons were prepared (3, 4 and 5 carbon links). The procedure used was identical to the first procedure provided above, in which the chloro-iodo alkylating agent was reacted in nitromethane with Vulcan XC-72 in the presence of aluminum trichloride. Elemental analysis showed the three alkylated carbons to contain 0.09, 0.09 and 0.10 mM chlorine/g carbon respectively.

3.1.5 Reaction of TAA with Functionalized Carbon

TAA was covalently bonded to the carbon surface by reacting the bis-N,N-dimethyl-aminomethyl TAA (Product B) with the functionalized carbon. In the general procedure, five molar equivalents (based on mM halogen/g carbon) of the bis-aminated TAA were reacted with the functionalized carbon for 48 hours in sulfolane at $100^\circ C$ under nitrogen. Following completion of this quaternization reaction, the reacted carbons were washed five times in methanol and harvested by centrifugation or filtration.

3.1.6 Metallating the Bonded TAA

The bonded TAAs were metallated with cobalt by reaction of the bonded carbon with ten molar equivalents of cobalt acetate (based on mM halogen/g carbon) in sulfolane at 100°C under nitrogen. The CoTAA-bonded carbons were then harvested and washed by repeated centrifugation with sulfolane, water, methanol and ether. The resulting structure, based on alkylated carbon, is diagrammed in Figure 3.2 (Product G).

This bonding procedure provided bonded-CoTAA levels with an average loading of 3% by weight of CoTAA. In those tests requiring higher CoTAA loadings, the bonded carbon was physically mixed 2:1 with sublimed CoTAA and heated in a quartz test tube under nitrogen for 16 hours at 420°C followed by one hour at 800°C (Product H). This heat-sintered material did not sublime at 270°C/0.5 mm showing that the bonded-CoTAA copolymerizes with the added CoTAA during heat-sintering.

3.2 Preparation of ^{14}C -Labeled Functionalized Carbons

3.2.1 Reaction with ^{14}C -Trimethylamine

Samples of the functionalized carbon types (Products C, D, E and F) in 20 weight volumes of methanol, were reacted with two molar equivalents (based on mM/g carbon) of ^{14}C -trimethylamine hydrochloride ($\text{C}_3\text{H}_9\text{NHCl}$; MW 96.5; 18.7 mCi/mg). Four equivalents of base (0.5% $^3\text{NaOH}$ solution) were added and the reaction was allowed to proceed for four days at room temperature. The ^{14}C -labeled carbons were harvested and washed by repeated centrifugation with methanol, water, phosphoric acid, nitromethane and ethyl ether.

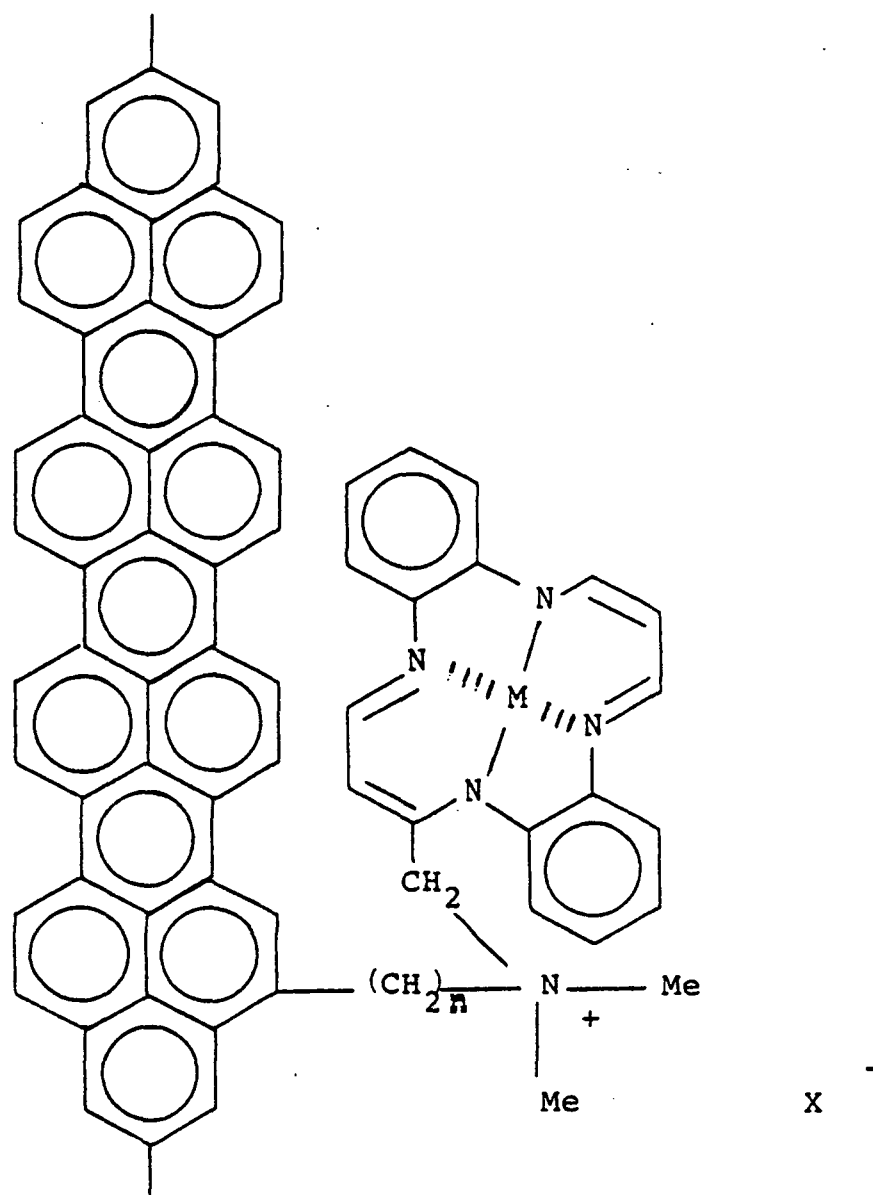
3.2.2 Reaction with ^{14}C -TAA

^{14}C -labeled bis-N,N-dimethylamino TAA ($\text{C}_{25}\text{H}_{29}\text{N}_6$; MW 470) was prepared following the procedure described in Section 3.1.1 using ^{14}C -labeled dimethylamine hydrochloride. The resulting ^{14}C -labeled bis-aminated TAA had an activity of 2.07×10^4 DPM/mM; it was reacted with the functionalized carbons following the procedure described in Sections 3.1.5 and 3.1.6 to provide metallated ^{14}C -labeled bonded-TAA carbons.

3.3 Synthesis of Bis-benzocyclobutene TAA

3.3.1 Synthesis Approach

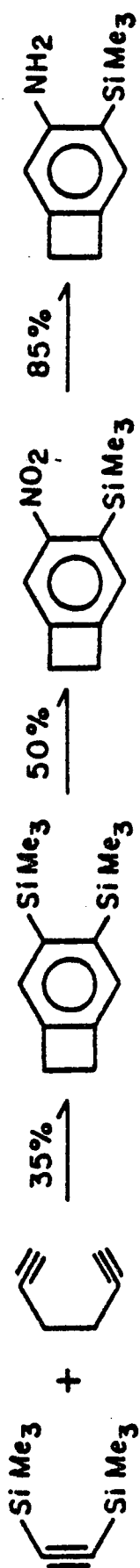
The synthetic steps are shown in Figure 3.3 with observed yields; the final product (XI; Product I) identified is but one example of a family of TAA-type monomers which could be made from the bis-aminobenzocyclobutene (IX; Product J). This one was chosen for initial evaluation because the diazo groups



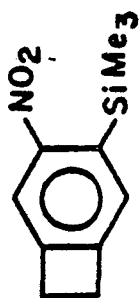
Carbon

Metallated TAA Moiety

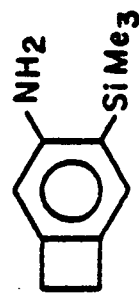
Figure 3.2 - The Structure of Metallated Alkylated Dibenzo Tetraaza-Annulene ($n = 3, 4, 5$ or 6)



III



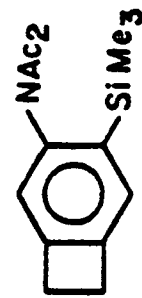
IV



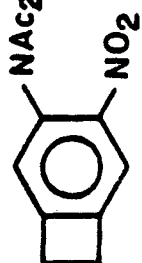
V



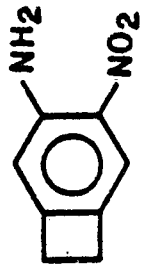
VI



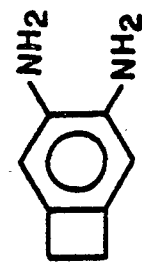
VII



VIII



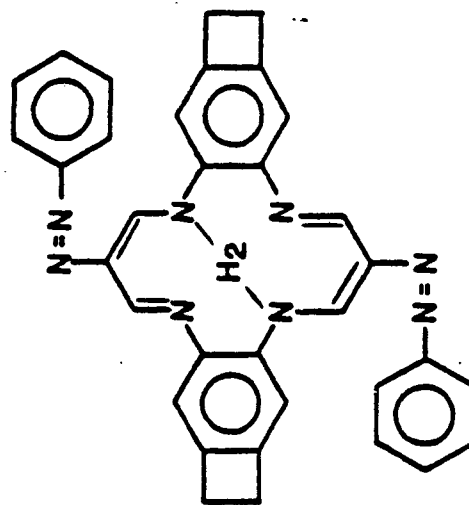
IX



X



XI

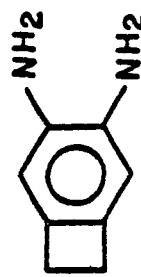


Product J

Figure 3.3

Product I

IX



are potentially heat liable, and would form radicals potentially capable of reacting directly with the carbon surface. This mechanism of bonding via radical reaction through heat sintering with an excess of bis-benzocyclobutene TAA was examined.

3.3.2 Preparation of Bis-benzocyclobutene TAA

In the synthesis of 4,5-bis(trimethylsilyl) benzocyclobutene [III; Ref: JACS 99: 4058(1977)], 1,5-hexadiyne (C_6H_6 ; MW 78) in bis(trimethylsilyl) acetylene (BTMSA; I) containing a catalytic amount of cyclopentadienyl cobalt dicarbonyl [$(C_5H_5)Co(CO)_2$; MW 180] was added via syringe pump to refluxing BTMSA (oil bath 140°) containing $(C_5H_5)Co(CO)_2$ under N_2 with magnetic stirring over 60 hours. At the end of this period, the pot was cooled, and excess BTMSA was distilled off on a vacuum line for reuse. The brown oily residue was chromatographed on silica with pentane. First cut gave the desired product as yellow crystals in 30-40% yield.

In the synthesis of 4-nitro-5-trimethylsilyl benzocyclobutene (IV), 4,5-bis(trimethylsilyl) benzocyclobutene (III) was dissolved in acetic anhydride with magnetic stirring and chilled in an ice bath for one-half hour. A two fold molar excess of 16 M nitric acid and a small volume of acetic anhydride were chilled separately in an ice bath, then the nitric acid was slowly added to the acetic anhydride [$(CH_3CO)_2O$; MW 102]. This $HNO_3/(CH_3CO)_2O$ solution was added to the chilled, stirred pot over 1 hour. The ice bath was removed, and the pot was refluxed 6 hours. The pot was cooled. Water and ether were added to extract the acetic anhydride. The upper ether layer was washed with $NaHCO_3$, H_2O , then dried over $MgSO_4$, filtered and rotovaped to a brown oil. This oil was chromatographed on silica with pentane. The first cut gave the desired product as light greenish crystals in 50% yield.

In the synthesis of 4-amino-5-trimethylsilyl benzocyclobutene (V), 4-nitro-5-trimethylsilyl benzocyclobutene (IV) was dissolved in benzene. One molar percent of 10% Pd/C was added to the pot and stirred at room temperature under H_2 at atmospheric pressure until hydrogen adsorption ceased. The catalyst was filtered off and the benzene rotovaped off to leave a brown oil that was the product in 85% yield.

In the synthesis of the 4-diaceto analog of (VI), 4-amino-5-trimethylsilyl benzocyclobutene (V) was refluxed in acetic anhydride for 3 hours. The reaction flask was cooled. Water and ether were added to extract the acetic anhydride. The ether layer was washed with $NaHCO_3$ and water, dried over $MgSO_4$, filtered and rotovaped to a brown oil. Chromatography on silica/methylene chloride gave a first cut, which upon solvent removal, yielded the desired product as white crystals in 70% yield.

The replacement of the 5-trimethylsilyl ligand with a 5-nitro ligand (VII) required synthesis of nitryl fluoride [FNO_2 ; via Inorg. Chem. 2 (1963) #6 Davis & Rausch]. The starting benzocyclobutene (VI) was dissolved in methylene chloride and chilled in a $\text{Et}_2\text{O}/\text{CO}_2$ bath. A $\text{Et}_2\text{O}/\text{CO}_2$ condenser was atop the reaction flask. FNO_2 (a 2x excess) was distilled into the flask and stirred for one hour. The $\text{Et}_2\text{O}/\text{CO}_2$ bath was removed so FNO_2 could reflux between the pot and condenser for one-half hour. Condenser was removed and any excess FNO_2 was allowed to escape. The methylene chloride was removed to leave an orange oil which was prep-plate^d on silica with 30% EtOAc/pentane. The third spot was the desired product, a yellow solid, in 20% yield.

In the synthesis of 4-amino-5-nitro benzocyclobutene (VIII), the starting benzocyclobutene (VII) was dissolved in glyme and refluxed with a tenfold molar excess of 0.5 N NaOH for 4 hours; the reaction vessel was cooled and the glyme/water was ether extracted. The ether layer was washed with water, dried over MgSO_4 , filtered, and rotovaped to obtain an orange solid which was the desired product in 90% yield.

In the synthesis of the desired 4,5-bis-aminobenzocyclobutene (IX; Product J), 4-amino-5-nitrobenzocyclobutene (VIII) was dissolved in THF and chilled in an ice bath for one-half hour. Aluminum amalgam was made by cutting an eight-fold molar excess of aluminum foil into squares, and dipping each successively for ten seconds in ether, abs. ethanol, 2% HgCl_2 in water, abs. ethanol, ether, then into the reaction vessel. When all the pieces were added, an excess of water was added. The pot was stirred in an ice bath for 18 hours. The grey solution was filtered; THF was rotovaped off to give the desired product in 80% yield. Product composition was verified by mass spectral and NMR data.

The final product (XI; Product J), shown in Figure 3.3, was prepared by reaction of IX with phenyl diazo malondialdehyde ($\text{C}_9\text{H}_8\text{N}_2\text{O}_2$; MW 176) [synthesized via Chem. Ber. 103: 1065 (1970)].⁹ The malondialdehyde was dissolved in a minimum boiling 95% ETOH; the bis-aminobenzocyclobutene (IX) was dissolved in 5:1 95% ETOH/glacial acetic acid and immediately added to the malondialdehyde solution. Pot solution turned red; reflux was continued for one-half hour. After cooling and filtering, the final product obtained was a red solid in 85% yield.

A second product made with 4,5-bis-aminobenzocyclobutene (IX; Product J) was the adduct formed by reaction with propargyl aldehyde. One molar equivalent of the bis-aminobutene (Product J) in five weight volumes of 1:1::ethanol:methanol were reacted for one hour at reflux under nitrogen with one molar equivalent of freshly prepared propargyl aldehyde. One molar equivalent of cobalt acetate (dissolved in ten weight volumes of

ethanol) was then added and the solution held at reflux for an additional half-hour. The desired metallated bis-aminobutene TAA (Product K) was harvested in 31% yield by filtration. The metallated analog of the bisdiazobenzocyclobutene was similarly prepared (Product L).

3.3.3 Preparation of Dimeric TAA

The metallated bis-benzobutene TAAs were polymerized to form dimeric TAA (planar TAA molecules held 'face-to-face' by two-carbon links) by heat sintering in the presence of Vulcan XC-72. In the heat-sintering procedure, the metallated bis-benzobutene TAA (either Product K or L) was mixed in a 1:2 ratio with Vulcan XC-72 and heat-sintered at 700°C under nitrogen for two hours. In the case of Product L, the diazo function was assumed to form a N radical which in turn reacted directly to the carbon surface.

3.4 Synthesis of ^{14}C -Labeled PTFE

3.4.1 Synthesis Procedure

A complete synthesis was carried out of PTFE on the scale required to provide ^{14}C -labeled material to monitor PTFE degradation in a cathode. The synthesis required four steps:

1. 35 mmole (0.945 g) of granular aluminum were amalgamated by washing in series with 40 ml each of ether, 5 % mercurous chloride, water and methanol. The amalgam was carefully added to 104 mmole (10 ml) of carbon tetrachloride (CCl_4) held at 0°C. The reaction mixture was then held at reflux for 30 minutes under nitrogen; following heating, the reaction mixture was cooled and poured into 150 ml of water; after further cooling, 150 ml of ether was added and the entire reaction mixture filtered. The organic layer was separated from the aqueous layer, washed with distilled water, dried over anhydrous magnesium sulfate (MgSO_4), and concentrated down to a brown solid. The solid was sublimed at 1 mm Hg/25°C to give 2.67 g (23 % yield) white hexachloroethane (C_2Cl_6 ; MW 237); identity was confirmed by IR.

2. 100 mmole (23.67 g) of hexachloroethane were mixed with 400 mmole (71.0 g) of SbF_3 and 7.5 ml of SbCl_3 in a 180 ml stainless steel bomb equipped with thermocouple, pressure gauge and valve. The bomb was sealed, heated at 300°C for 40 hours and then cooled to room temperature. The volatile contents of the bomb were distilled into a -78°C trap (52 % yield); IR of this gas confirms it to be $\text{C}_2\text{Cl}_2\text{F}_4$ (MW 171).

3. Zinc dust was cleaned by washing with 10 % HCl for two minutes followed by rinsing with water, acetone, and air drying. 306 mmole (20 g) of cleaned zinc dust were added to a 75 ml stainless steel bomb containing 40 ml abs. ethanol, 50 mg

zinc chloride (ZnCl_2); the bomb was then cooled to -196°C with liquid nitrogen and 144 mmole (24.6 g) of $\text{C}_2\text{Cl}_2\text{F}_4$ distilled into it. The bomb was sealed, warmed to 110°C and rocked for 40 hours. The bomb was cooled and 24 mmole of tetrafluoroethylene (TFE) [C_2F_4 ; MW 100] recovered (17 % yield); identity was verified by IR.

4. 25 mmole of TFE were distilled into a 75 ml stainless steel bomb loaded with 50 ml deoxygenated water and 100 mg ammonium persulfate [$(\text{NH}_4)_2\text{S}_2\text{O}_8$]. The bomb was rocked and heated at 80°C ; a bomb pressure decrease from 380 psi to 120 psi was observed over two hours. The bomb was cooled, pressure released and 3.3 g of PTFE (Product M) recovered (99 % yield) by filtration; IR confirmed the identity.

When this synthesis was repeated on a one quarter scale using ^{14}C -labeled carbon tetrachloride, 900 mg of ^{14}C -labeled PTFE were obtained (Product N). Combustion analysis of the product by New England Nuclear showed the material to have an activity of 68,000 DPM/mg.

The resulting ^{14}C -labeled was mixed with commercially available PTFE to form the wet-proofing layer in the primary fuel cell cathodes tested.

4.0 Evaluation of Carbon Functionalization Methods

4.1 Introduction

Three carbon functionalization procedures (acylation, cycloaddition, alkylation) were used to covalently link the TAA catalyst to the carbon surface. The stability of these links was evaluated by stressing the functionalized carbons and measuring either the rate of release of the bonded material or the change in electrochemical activity of the catalyzed carbon. The rate of material release was measured based on change in carbon surface content of ^{14}C -labeled material. The change in electrochemical activity was measured directly using cyclic and pulsed voltammetry.

4.2 Release of Bonded Material

4.2.1 Rate of ^{14}C Release Based on ^{14}C -trimethylamine

The four functionalized carbons (Products C - F) were reacted with two molar equivalents of ^{14}C -trimethylamine (Section 3.2.1). 100 mg samples of these four carbons (as well as a control of Vulcan XC-72 which had been treated with a similar amount of ^{14}C -trimethylamine) were treated in 85% phosphoric acid in capped quartz test tubes; one series of tubes was held at room temperature and the other at 150°C . After 30 days the carbons were collected by centrifugation and samples were sent to New England Nuclear for analysis. The results obtained, as well as the DPMs (degradations per minute) measured in the phosphoric acid, are provided in Tables 4.1 and 4.2.

The results obtained show that the treatment at 150°C removes the majority of the label from all the carbons. The distribution of this label between the solution and gas phases potentially could provide insight as to the degradation mechanisms and indicate whether the linking ligand or the quaternary ammonium bond formed between the ligand and the amine is unstable: if the quaternary ammonium bond were attacked, a volatile product would be obtained (methyl bromide) with a probability of one third of the labeled methyl functionality being released. This possibility can not be dismissed given the data provided in Table 4.2. The original research plan had called for labeling polystyrene via a quaternary ammonium bond and evaluating it as a control; this material proved to be unstable in heated phosphoric acid.

The results obtained in these labeling-aging experiments were therefore inconclusive; a second series of experiments was undertaken based on reacting the functionalized carbons with ^{14}C -labeled TAA.

Table 4.1

DPMs/mg-Carbon at Room Temperature
for ^{14}C -Labeled Amine

<u>Carbon Type</u>	<u>Vulcan</u>	<u>Acylated (Product C)</u>	<u>Cycloaddition (Product D)</u>	<u>Alkylation #1 (Product E)</u>	<u>Alkylation #2 (Product F)</u>
DPM/mg at start	6308	52471	4269	6011	5923
DPM/mg after 30 days	5524	43519	2542	4835	4509
% remaining	87.6	82.9	59.6	80.4	76.1
DPM/mg in solution	999	4247	263	759	1153
% lost	----	9.0	34.2	7.0	4.4

Table 4.2

DPMs/mg-Carbon at 150°C
for ¹⁴C-Labeled Amine

<u>Carbon Type</u>	<u>Vulcan</u>	<u>Acylated (Product C)</u>	<u>Cycloaddition (Product D)</u>	<u>Alkylation #1 (Product E)</u>	<u>Alkylation #2 (Product F)</u>
DPM/mg at start	6308	52471	4269	6011	5923
DPM/mg after 30 days	144	9420	362	1342	1808
% remaining	2.3	18.0	8.5	22.4	30.5
DPM/mg in solution	2264	19159	400	4375	3527
% lost	61.8	45.5	82.1	5.8	10.0

4.2.2 Rate of ^{14}C -Release Based on TAA

Five molar equivalents (four unlabeled and one ^{14}C -labeled) of bis-dimethylamino TAA were reacted with each functionalized carbon for 48 hours at 100°C in sulfolane under nitrogen as described in Section 3.2.1; a control of Vulcan XC-72 was also run. After vacuum drying, 5 mg samples were sent to New England Nuclear for DPM analysis; the remaining 50 mg were held at 150°C in 85% phosphoric acid for 33 days. The acid was sampled after 2, 7 and 30 days to determine DPM in solution; the acid-treated carbon was harvested by centrifugation and 5 mg samples were sent to New England Nuclear for DPM analysis.

Table 4.3 provides the analysis results on the five carbons. The link based on alkylation (Products E and F) provides the highest bonding TAA efficiency; however, the percent label remaining on the carbon surface is similar after acid treatment for all carbon functionalization types. The percent label lost through volatilization brings into question whether bonding of the TAA has actually occurred: if the bis-dimethylamino TAA is adsorbed to the surface, it would desorb with washing providing a low bonding efficiency; under acid conditions, the remaining adsorbed bis-dimethylamino TAA would deaminate and the resulting amine would slowly volatilize giving an increased percentage lost of ^{14}C label. Bonded (quaternized) material would not deaminate and therefore a low percentage lost would be obtained. This analysis indicates that bonding of the TAA has occurred using the alkylation procedures based on the low percentage lost shown for the alkylation procedures in Table 4.3.

The stability of the link formed using alkylation is high, as shown by the solution DPM data provided in Table 4.4. These data show a rapid increase in counts in solution for the first few days due to desorption, followed by a very slow increase for the following twenty-six days. These data indicate that a stable bond between the carbon surface and the alkyl link is obtained. Further validation of bond stability will require significantly increased test periods.

4.3 Electrochemical Activity

4.3.1 Cyclic Voltammetry Evaluation

4.3.1.1 Introduction

Cyclic voltammetry was used when a rotating disk evaluation technique did not provide useful data. The cyclic voltammetry technique entailed subjecting a catalyzed electrode to a linear voltage triangular ramp and recording the resulting changes in current with respect to voltage. The current-voltage recording, termed a voltammogram, illustrated the electrochemical

Table 4.3

DPMs/mg-Carbon at 150°C
for ¹⁴C-Labeled TAA

<u>Carbon Type</u>	<u>Vulcan</u>	<u>Acylated (Product C)</u>	<u>Cycloaddition (Product D)</u>	<u>Alkylation #1 (Product E)</u>	<u>Alkylation #2 (Product F)</u>
DPM/mg	-----	1.42x10 ⁵	0.24x10 ⁵	0.62x10 ⁵	0.97x10 ⁵
DPM/mg start	4.27x10 ³	3.68x10 ³	2.25x10 ³	1.29x10 ⁴	1.45x10 ⁴
Bonding Efficiency %	-----	2.6	5.4	20.8	15.0
DPM/mg 33 days	1.05x10 ³	0.93x10 ³	0.62x10 ³	4.19x10 ³	4.85x10 ³
% Remaining	-----	25.3	27.6	32.5	33.4
DPM/mg in solution	2.46x10 ³	1.65x10 ³	1.12x10 ³	6.59x10 ³	7.26x10 ³
DPM/mg lost	0.76	1.10x10 ³	0.51x10 ³	0.21x10 ³	0.24x10 ³
% lost	17.8	29.9	22.7	1.6	1.7
Sites, μM/mg	-----	.183	.031	.079	.124

Table 4.4

DPMs in Solution		<u>Days</u>	
<u>Carbon</u>		3	7
<u>% of DPMs Initially Bonded on Carbon Surface</u>			
Alkylation #1 (Product E)	33	39	41
Alkylation #2 (Product F)	37	43	49

reactions that take place in the system at various potentials over the preselected potential range. By purifying the system of undesirable reactants, the voltammogram describes solely the reactions associated with the catalyst.

In the case of the CoTAA electrodes, the $\text{Co}^{+3}\text{TAA}/\text{Co}^{+2}\text{TAA}$ redox couple is the one of interest. The quantity of CoTAA present on the catalyst surface can be quantitatively determined based upon a relationship derived by Fred Anson et al. [Anal. Chem. 50:227 (1978)]

$$i_f = \frac{n^2 F^2}{4RT}$$

where i_f = faradaic current arising from the redox couple
 = surface coverage
 = geometric surface area
 = scan rate

The faradaic current can be determined geometrically using the cyclic voltammogram after accounting for the systems' capacitive current. Eight CoTAA-bonded carbon pellets (four fresh and four acid-treated carbons) were subjected to this cyclic voltammetry analysis.

4.3.1.2 Pellet Fabrication

A new procedure was developed to test 50 mg quantities of catalyst for catalytic activity.

Blank pellets containing 70% Vulcan XC-72 and 30% PTFE (Dupont #6) were pressed in a stainless steel, 3 piece compression mold at 320°C and 27,000 psi for 1 hour. After this sintering time, the pellet remained under pressure and the mold cooled to room temperature. The resulting pellets were bullet-shaped: they were 1 cm in diameter at the base and tapered to a flat surface, 0.6 cm in diameter at the tip. These pellets were electrically very conductive; mechanically, they resembled hard rubber. They were quite porous.

A special Teflon holder, shown in Figure 4.1, was developed to retain the test pellets. This holder screwed onto a threaded Teflon shaft and thereby pressed the bullet-shaped pellet firmly against a coil of platinum wire which affords electrical contact to the outside. Once placed into the holder, a 0.28 cm² pellet tip was exposed to the electrolyte. A diagram of the complete test cell is shown in Figure 4.2.

The test pellets were individually placed into the Teflon holder and then into the test cell. The reference electrode was a dynamic hydrogen electrode held in a quartz Luggin capillary tube; the counter electrode consisted of a piece of pure platinum wire held in a quartz tube. The electrolyte (2M H₃PO₄) was degassed by bubbling nitrogen through it, prior to and during,

Figure 4.1: Pellet Holder

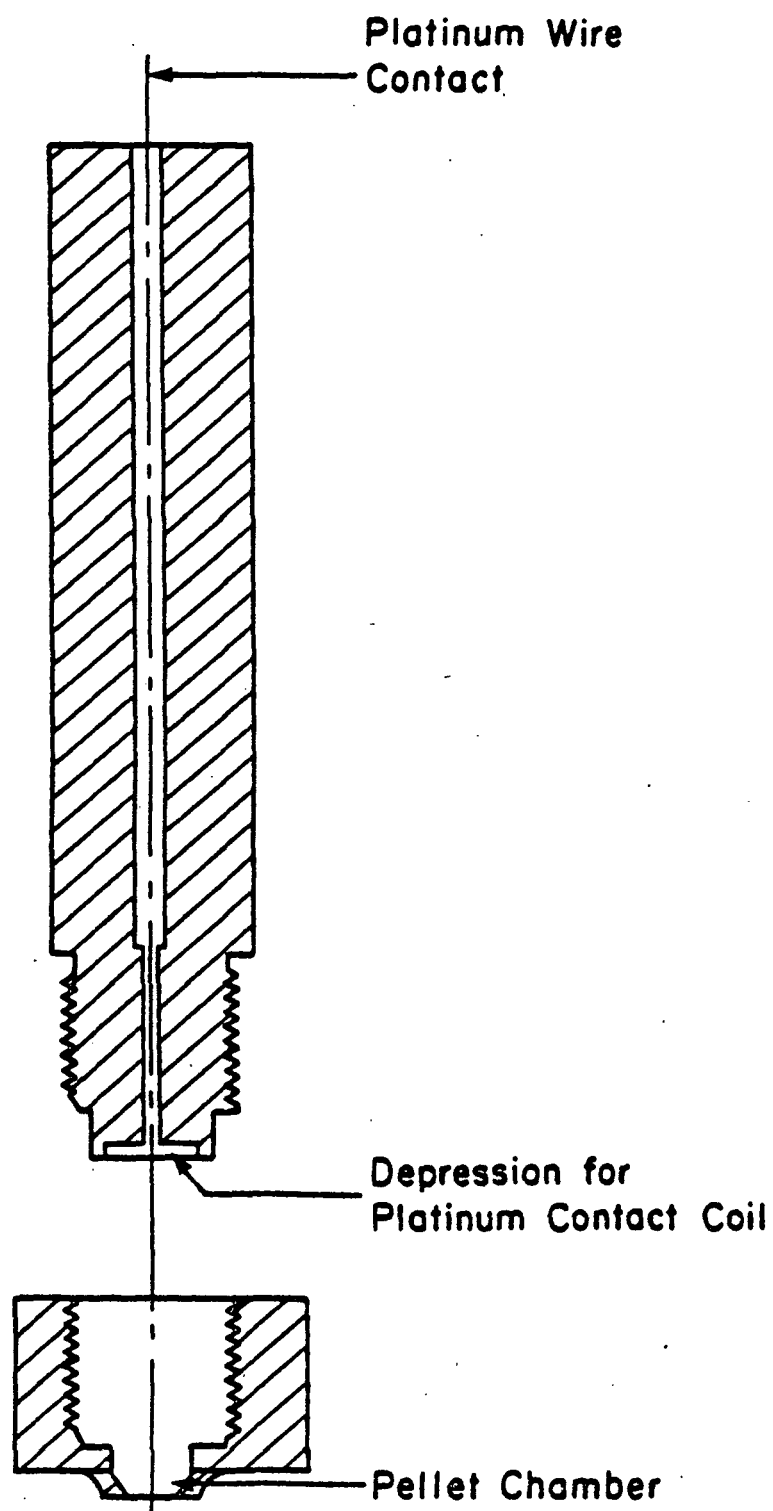
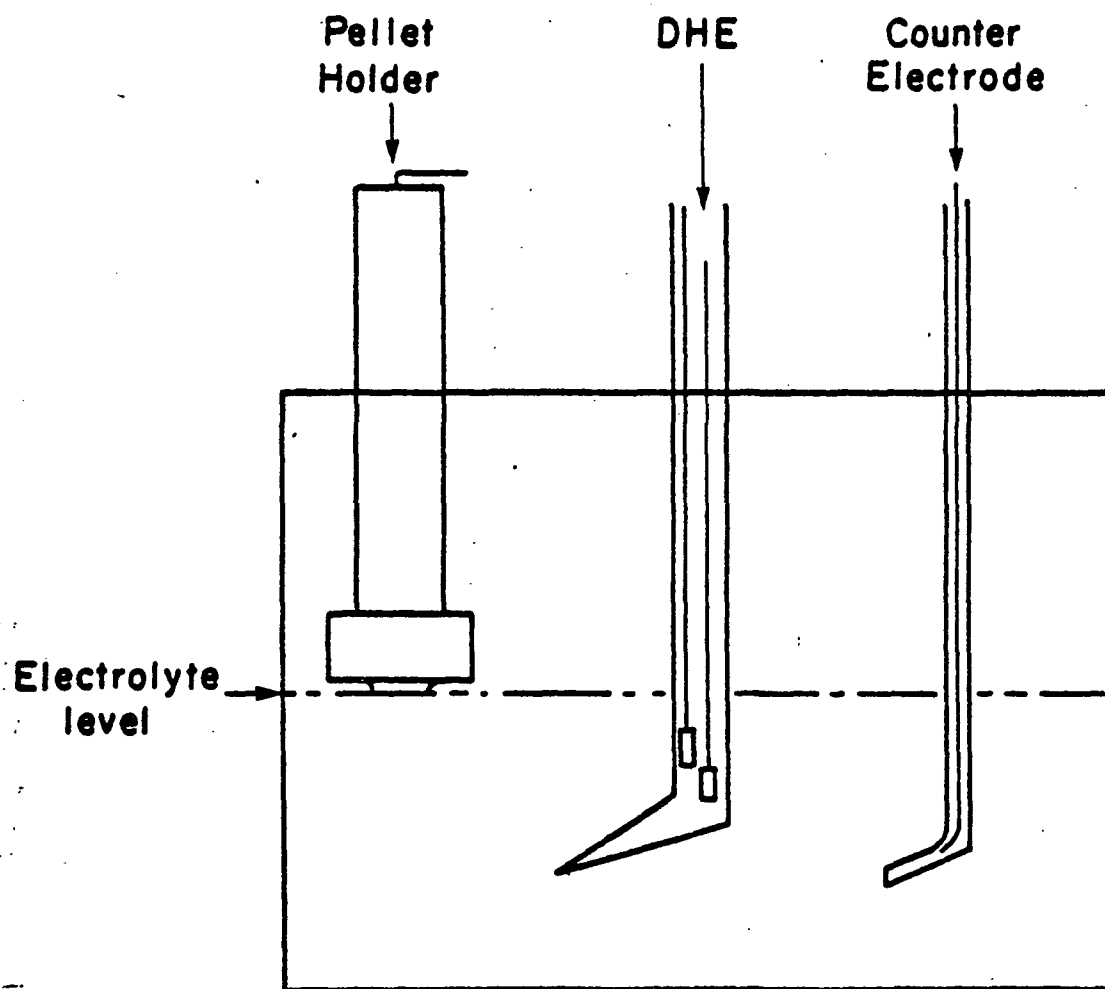


Figure 4.2: ECO Cyclic Voltammetry Test Cell



each test run. The electrolyte was stirred using a magnetic stirrer during degassing and testing.

Each pellet, and the controls, were subjected to a series of triangular voltage ramps from +0.1 V to +1.5 V vs DHE at a scan rate of 1.2 V/min. Several sweeps were recorded to ensure reproducibility after which a representative sweep was obtained. An AMEL Model 472 WR Multipolarograph was used for all of the tests and the data were recorded using an HP 7045A X-Y Recorder. The controls included a pure Vulcan XC-72 pellet, a platinized platinum electrode, and a platinum-tipped Vulcan XC-72 pellet electrode.

4.3.1.3 Cyclic Voltammetry Results

Provided in Table 4.5 are the results of the test procedure: anodic current, i_a , is shown for the eight pellets tested. Based on the observed currents, the activity of all four untreated CoTAA-based carbons is equal; acid treatment for 31 days in 150°C 85% phosphoric acid significantly reduces the activity of the cycloaddition bonded catalyst, and does not affect the activity of the alkylation bonded catalyst. These results confirm the results on release of ^{14}C from ^{14}C -labeled bonded TAA.

4.3.2 Pulsed Voltammetry Evaluation

4.3.2.1 Introduction

Differential pulsed voltammetry on solid stationary electrodes is analogous to differential pulse polarography on the dropping mercury electrode. Both techniques involve superimposing a small D.C. voltage pulse on a linear D.C. voltage ramp, and measuring the generated current at two intervals during each pulse. The difference between these two currents is determined instrumentally, and is plotted vs potential on an X-Y recorder as a pulse voltammogram. Pulse voltammetry offers improved sensitivity by clearly defining faradaic current peaks which are sometimes obscured in normal D.C. voltammetry.

4.3.2.2 Procedure

Each pellet prepared, as described in Section 4.3.1.2, was placed in the special Teflon holder shown in Figure 4.1. This holder was inserted into a test cell filled with deaerated 85% H_3PO_4 . The necessary electrical connections were made, and the pellet was subjected to pulse voltammetry vs a DHE at room temperature and subsequently at 100°C. A platinum wire constituted the counter electrode. Pulse voltammetry was repeated until reproducibility was obtained (usually 2-3 sweeps), and peak current was measured at +590 mV (anodic) and at +430 mV (cathodic). Reproducible cyclic voltammetry was run on each pellet just prior to pulse voltammetry to aid in data

Table 4.5 Faradaic Current for Bonded-CoTAA
Catalyzed Pellets

<u>CoTAA Bond Type</u>	<u>Acid Pretreatment</u>	<u>i_f, mA</u>
Acylation (Product C)	no	10
Acylation	yes	8.4
Cycloaddition (Product D)	no	11
Cycloaddition	yes	0
Alkylation (via AlCl_3 , Product E)	no	11
Alkylation	yes	11
Alkylation (via K/naph., Product F)	no	11
Alkylation	yes	11

interpretation.

4.3.2.3 Results

Pulsed voltammetry evaluation was made of the pellets which had been made previously of functionalized CoTAA-catalyzed carbons and had been acid-treated at 150°C in 85% phosphoric acid for a month. The results obtained are shown in Table 4.6. Previous analysis of these carbons based on measurement of the anodic current in cyclic voltammetry had shown that of the four bonding methods (acylation, cycloaddition, alkylation via AlCl_3 and alkylation via K/naphthalene), the cycloaddition bond was not stable and the alkylation procedures appeared to be more stable than the acylation procedure. These results were also verified based on release of radioactivity from ^{14}C -labeled TAA. The results provided in Table 4.6 again verify these findings.

4.4 Summary

Based on the results obtained using release rates of ^{14}C -labeled material and electrochemical activity after stressing for a month in 150°C 85% phosphoric acid, the alkylation procedure of carbon surface functionalization provides a carbon-catalyst link of greater stability than the links formed by either acylation or cycloaddition.

Table 4.6

Pulse Voltammetry Data on TAA-Catalyzed Pellets
as a Function of Bond Type at Room Temperature

<u>Bond Type</u>	<u>Peak Current Density, mA/cm²</u>			
	<u>Acid Treatment:</u>	yes	no	% change
Acylation		41.3	47.5	15
Cycloaddition		0	57.5	100
Alkylation (AlCl ₃)		51.0	52.5	3
Alkylation (K/naph.)		46.3	46.3	0

5.0 Evaluation of Electrocatalytic Performance of the Alkylation Bond

5.1 Effect of Variation in Link Length

5.1.1 Cathode Preparation

Wet-proof cathodes were prepared by depositing 100 mg of 30%/70% Teflon/catalyzed carbon on a support of stiff carbon fabric (PWB-35; Stackpole Fibers) containing a thin layer (100 mg) of 30%/70% Teflon/Vulcan XC-72. The matrix was placed on a gold-plated expanded tantalum screen and pressed at 320°C/1000 psi for 5 min. Two control cathodes were prepared: an uncatalyzed Vulcan XC-72 cathode and a 10% platinum on carbon catalyzed cathode (Prototech; 50-25 A crystals; 120-150 m²/g).

5.1.2 Short-Term Fuel Cell Tests

Five types of catalyzed cathodes were tested in the ECO fuel cell (Figure 5.1) in 100°C 85% phosphoric acid. After initial performance evaluation, the cathodes were held at + 650 mV vs DHE for 100 hours and performance was again evaluated. The five cathode types were 10% platinum on carbon, 33% CoTAA on Vulcan XC-72 (Product H), 33% CoTAA on Vulcan XC-72 reacted to have CoTAA linked via a three carbon link on the surface, 33% CoTAA on Vulcan XC-72 with four-carbon linked CoTAA, and 33% CoTAA on Vulcan XC-72 with five-carbon linked CoTAA. All the CoTAA-containing carbons were sintered for two hours under nitrogen at 700°C prior to cathode fabrication; the alkylation procedure was used to provide the carbon links, as described in Sections 3.1.4 and 3.1.6.

Provided in Figure 5.2 is a Tafel plot for the IR-free data obtained for the platinum control and for the 33% CoTAA sintered on three-carbon linked CoTAA-Vulcan XC-72. Provided in Table 5.1 is a summary of the IR-free performance data obtained for the five cathode types after stressing for 100 hours in 100°C 85% phosphoric acid at + 650 mV vs a DHE. Based both on the Tafel slope (mV/decade) and on the absolute magnitude of the potential at 10 mA/cm² using 99.9% oxygen as the fuel, all of the sintered CoTAA (linked or non-linked) cathodes show significantly improved performance compared to the 10% platinum-catalyzed cathode; the dimeric-CoTAA catalyzed cathode showed performance similar to platinum. The rest potential of all the CoTAA-catalyzed cathodes was approximately 130 mV lower than that of the platinum catalyzed cathode.

During the 100 hour stress period, the performance of none of the five cathodes shown in Table 5.1 showed any significant change (less than 1%). One of the cathodes (C-4/CoTAA) was allowed to continue for an additional 900 hours. During this extended test period, the performance of this cathode was observed to decay uniformly to a total loss of 22%. Raising the

Figure 5.1 The ECO Fuel Cell

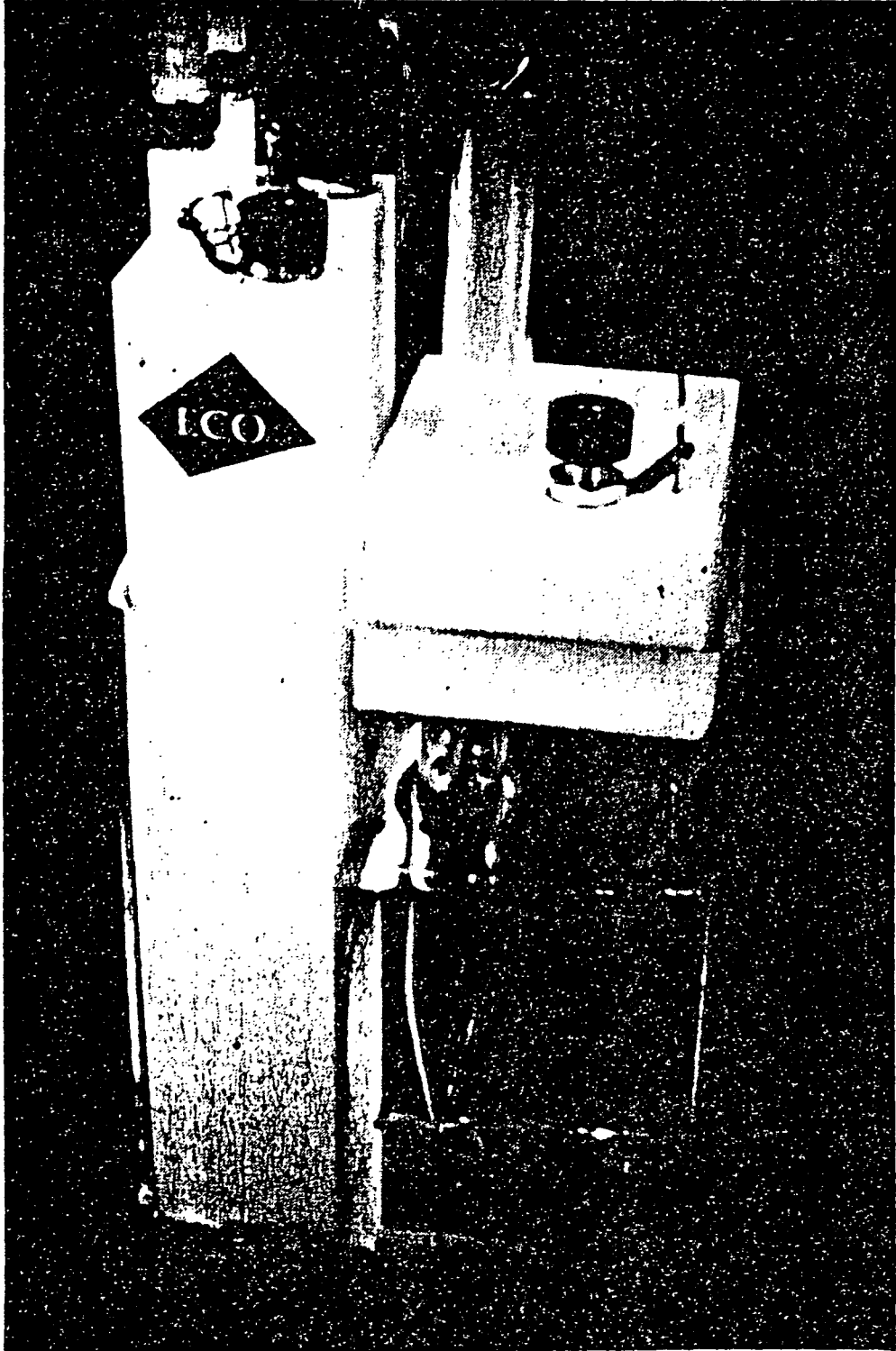


Figure 5.2: Electrode Performance at 100 °C in 85% H₃PO₄
After 100 Hours.

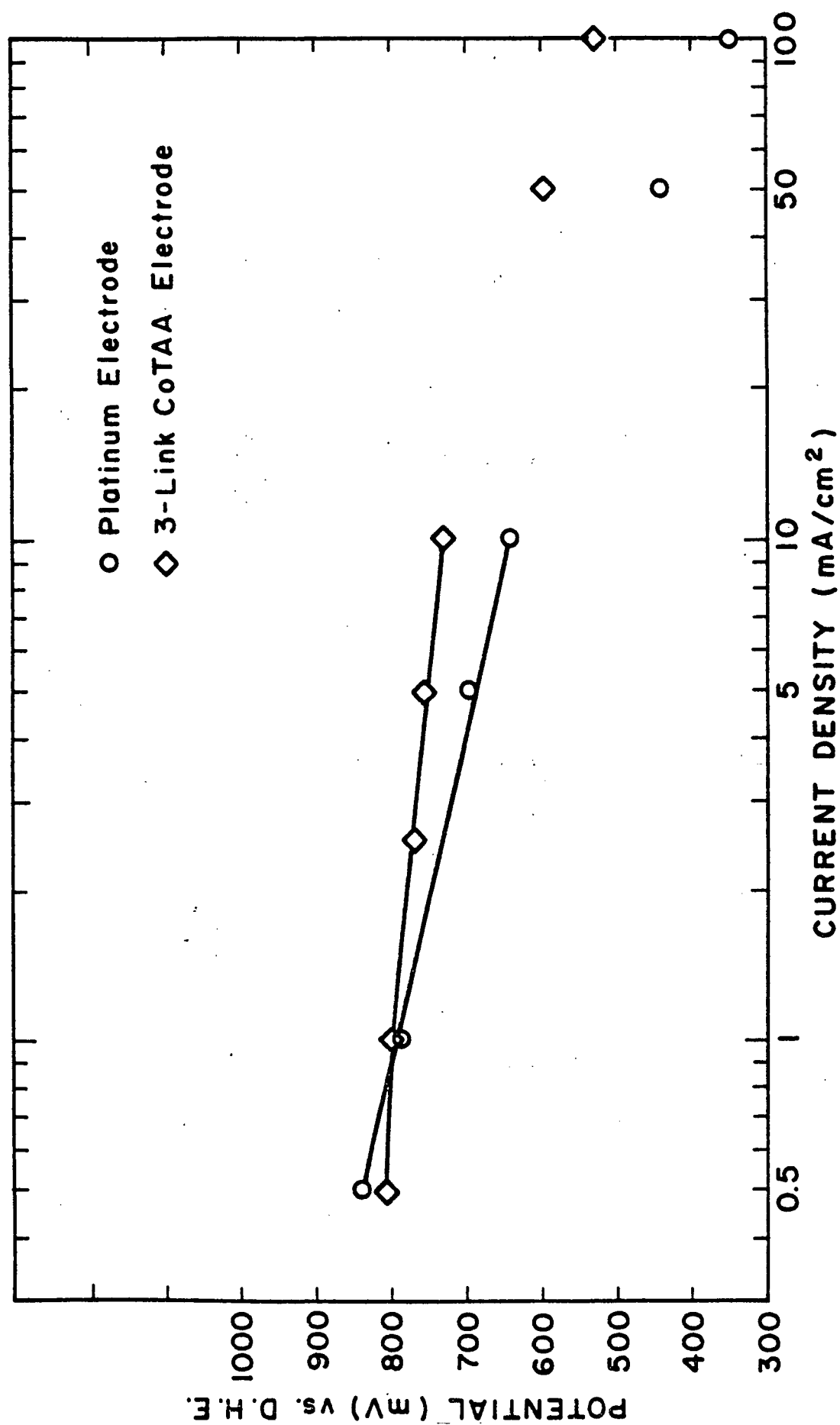


Table 5.1

Performance of Various Cathodes
after 100 hours*

<u>Catalyst</u>	<u>Rest Potential in O₂ at 100°C (mV)</u>	<u>Tafel Slope at 100°C (mV/decade)</u>	<u>Potential at 10 mA/cm² (mV)</u>
Platinum	960	130	640
CoTAA	830	60	758
C-3/CoTAA	833	60	750
C-4/CoTAA	840	60	740
C-5/CoTAA	816	50	730

* Cathodes held at 100°C at 650 mV vs DHE during test period.

temperature to 125°C for the bonded cathodes (C-4, C-5) or the unbonded CoTAA resulted in increased decay in performance (21%, 46% and 68% respectively) in approximately 100 hours. Based on the observation that the electrolyte was colored a dark amber when increased decay was observed, the C-3 cathode was tested under a different condition. For this cathode, the electrolyte contained 3 mg/ml of cobalt phosphate ($\text{Co}_3(\text{PO}_4)_2 \cdot 8\text{H}_2\text{O}$); the cathode was stressed at 125°C in 85% phosphoric acid and + 650 mV vs DHE. After 100 hours at these conditions, no performance decay was observed. This suggests that the performance decay mechanism is dissolution of the cobalt species from the organo metallic complex.

5.2 Effect of Fuel Variation

An examination was made of the effect of using compressed air rather than oxygen as the fuel source. Three cathodes were examined: a commercially available platinum catalyzed cathode (RA2-Prototech, Inc., Newton Highlands, MA), a platinum catalyzed cathode made at ECO (10% platinum on carbon), and a C-5/CoTAA catalyzed cathode. These latter two cathodes were prepared as described in Section 5.1.1 above.

The cathodes were tested at 100°C in 85% phosphoric acid. The results obtained are provided in Table 5.2; these results show that the platinum catalyzed cathodes have a rest potential loss from using air rather than oxygen which is on the order of 70 mV; the C-5/CoTAA does not have such a loss. This difference in loss is also observed under load when the two ECO prepared cathodes are compared. Thus, CoTAA catalyzed cathodes do not appear to suffer similarly from decreased performance compared to platinum catalyzed cathodes when air is used as the fuel.

5.3 Summary

The results obtained in half-cell tests show no significant difference in performance of cathodes catalyzed with CoTAA where the CoTAA is bonded to the carbon support surface by varying length alkyl links. The bonded catalyst is shown to have performance superior to platinum at 100°C based both on Tafel slope and potential under load. Cathodes catalyzed with TAA also do not show the performance loss when air is used as a fuel rather than oxygen.

Table 5.2

Cathode Performance on Air vs Oxygen*

<u>Cathode</u>	<u>Potential, mV</u>				
	<u>Load, mA/cm²</u>	0		2.5	
	<u>Gas</u>	<u>O₂</u>	<u>Air</u>	<u>O₂</u>	<u>Air</u>
RA2-Pt		974	894	886	828
Pt		884	828	740	640
C-5/CoTAA		828	828	784	744

* at 100°C in 85% phosphoric acid; potential measured vs DHE.

6.0 Stability of Polytetrafluoroethylene

6.1 Introduction

One of the major objectives of the program was to evaluate the stability of polytetrafluoroethylene (PTFE) under primary fuel-cell conditions. During the program, two tasks were carried out which showed significant changes in PTFE based on observed physical and chemical-based parameters. In the first task, films of commercially available PTFE were chemically stressed in 200°C phosphoric acid and electrochemically stressed in 150°C phosphoric acid. In the second task, ¹⁴C-labeled PTFE was prepared, incorporated in a platinum catalyzed cathode, and the cathode held under load in a half-cell using oxygen as a fuel; the release of ¹⁴C was used to identify PTFE chemical change.

6.2 Stressing of PTFE Films

6.2.1 Film Fabrication Procedure

Film fabrication methods used to make the PTFE films resemble powder metallurgy. Four commercially available powders were obtained for testing: DuPont Teflon 6; ICI Fluon G-307; Allied Chemical Halon G-80 and Hoeschst Hostaflon TF 1620.

Approximately one-half gram of the powder was placed onto a polished stainless steel disk; sieving was not necessary. The granules were pressed under light pressure of approximately 1,000 psi at room temperature except for the DuPont Teflon which was pressed at 300 psi. This preform was placed into a preheated Glas-Col Heating Mantle Model #TM-614 where the film was polymerized by sintering at approximately 380°C. An Electro-Flex Model F5000 temperature controller maintained the necessary sintering temperature. After the preform became a transparent gel-like film, the heating mantle was shut off and the film was cooled slowly to prevent cracking and to inhibit brittleness. A physical change in the powder, from opaque to transparent, was observed through a Kimax cover which rested on top of the heating mantle. Slow cooling decreased the degree of film shrinkage.

After the films cooled, final samples were obtained by using a punch to remove a small area from the innermost portion where gelling had occurred.

The four samples were evaluated: acid contact angle and direct IR testing was performed. Table 6.1 provides physical data on the disks before stressing.

6.2.2 Chemical Stressing

The PTFE samples were acid-stressed in specially

Table 6.1 Physical Data on PTFE films

Characteristic

Diameter, cm	1.32
Area, cm ²	1.37
Thickness, mm	0.80
Weight, mg	200

prepared quartz incubators with 5 ml of 85% H_3PO_4 . Specially machined Teflon plugs sealed each vessel upon heating. The quartz vessels were maintained at 200°C with a Glas-Col Heating Mantle #TM-614 and a variable autotransformer. The Teflon caps were wired to the tubes to prevent accidental popping due to pressure. The samples were subjected to this hot H_3PO_4 treatment for over 3500 hours during which test period they were removed periodically and again subjected to direct measurement of contact angle and IR.

The procedure used for measuring contact angles was similar to that used by Fox and Zisman [J. Colloid Sci. 5: 514 (1950)]. The measurements were made at room temperature and atmospheric pressure using a Gaertner M101 telescope fitted with a M205 protractor eyepiece. The procedure consisted of placing a single drop of 85% phosphoric acid on the PTFE film which, in turn, was sitting on a horizontally positioned holder. The telescope was focused on the drop and the contact angle between the drop and the film measured. Error in this measurement was $\pm 1.3^\circ$ based on 10 independent measurements. IR measurements were made directly on the film using a Perkin-Elmer Model 727 infrared spectrophotometer.

The results obtained on changes in wetting angle are provided in Table 6.2. These data show that for the first 2000 hours, no significant change in wetting was observed; in the next 1500 hours, significant wetting angle changes were observed. No significant changes in film IR were observed during the test.

6.2.3 Electrochemical Stressing

A second series of films was prepared from the commercially available PTFE powders, as described in Section 6.2.1; these films were held in close contact to slightly smaller diameter disks of vitreous carbon by wrapping with platinum wire. The disks were held in oxygenated, 150°C 85% phosphoric acid; a constant load was applied to hold the carbon disks at + 200 mV vs DHE.

Three series of films were prepared and tested. The average results on observed wetting angle are provided in Table 6.3. This effect of electrochemical stressing appears to be an acceleration of the change in surface wetting angle observed with chemical stressing. Again, no change in film IR was observed.

6.2.4 ESCA Surface Evaluation

Samples of the original film, Hoeschst Hostaflon #1620 and the material after it which had been electrochemically stressed for over 1400 hours, were evaluated by Electron Spectroscopy for chemical analysis (ESCA) by PhotoMetrics, Inc.

(Woburn, MA). The results of this evaluation are provided in Figures 6.1 and 6.2; these results show that significant PTFE surface chemistry changes occur as it is stressed in hot phosphoric acid.

The stressed film shows evidence of increased C-O bonding both in the carbon narrow scan (Figure 6.1) and oxygen narrow scan (Figure 6.2). The stressed film shows slightly more (CHF-CF_2) groups and also has approximately two times the amount of hydrocarbon - like carbon (284.6 eV). The stressed film also shows evidence of (CHF-CH_2) grouping (shoulder on 284.6 eV peak at 285.0 eV). The shoulder on the 285.0 eV peak is carbon bound to O and C-O.

6.3 PTFE Stressing in Half-Cell Cathodes

6.3.1 Cathode Preparation and Test Procedure

Two cathodes were prepared using a 5 or 10% ($^w/w$) mixture of ^{14}C -PTFE (prepared as described in Section 3.4) with DuPont Teflon #6 (Cathodes Pt #4 and Pt #5). A control cathode was also prepared using only the DuPont PTFE. All three cathodes were platinum-catalyzed (10% Pt on carbon; Prototech; 50-25 A crystals; 120-150 m^2/g) and prepared as described in Section 5.1.1. The cathodes were tested in half-cells on oxygen in 125°C 85% phosphoric acid; they were held at constant load during the test period (+ 650 mV vs DHE). One ml aliquots of the electrolyte (75 ml) were removed on a periodic schedule (one day, three days, seven days and monthly thereafter) and evaluated for released ^{14}C -label. At the end of the test period, samples of the cathodes, as well as initial samples, were sent to New England Nuclear for specific activity (DPM/mg) evaluation.

6.3.2 Results

The two cathodes (Pt #4 and Pt #5) were tested for 4000 and 2000 hours, respectively. During this test period, no significant changes in electrolyte ^{14}C specific activity was observed; the performance of all three Pt-catalyzed cathodes was observed to be similar during the test periods, with only small performance decays observed (less than 5%). A significant change in cathode ^{14}C specific activity was observed, as shown in Table 6.4: specific activity is observed to decrease on the order of 10% in both cathodes.

These results combined with the ESCA results support the PTFE degradation mechanism presented in Figure 6.3. The PTFE identified in the figure has a carboxyl polymer chain end-group [M.I. Bro and C.A. Sperati, J. Polymer Sci., 38: 289 (1959)]. Under the elevated temperatures and acidic conditions of the primary fuel cell, this carboxyl can be degraded to release CO_2 and HF. The former product would not remain in the electrolyte (ie: no ^{14}C -activity), but a decrease in specific activity of the

Table 6.2

Effect of 200°C Phosphoric Acid on
PTFE Film Wetting Angle

<u>Time, hrs.</u>	0	2160	3570
<u>PTFE Source</u>			
Allied Halon G-80	112°	112°	106°
DuPont #6	117°	114°	107°
Hoechst Hostaflon #1620	120°	118°	107°
ICI G-307	117°	117°	108°

Table 6.3

Effect of 150°C Phosphoric Acid and + 0.2 V vs DHE on
PTFE Film Wetting Angle

<u>Time, hrs.</u>	0	720	1440
<u>PTFE Source</u>			
Allied Halon G-80	112°	111°	108°
DuPont #6	117°	109°	107°
Hoechst Hostaflon #1620	120°	108°	107°
ICI G-307	117°	109°	105°

Figure 6.1: Carbon Scan - ECSA

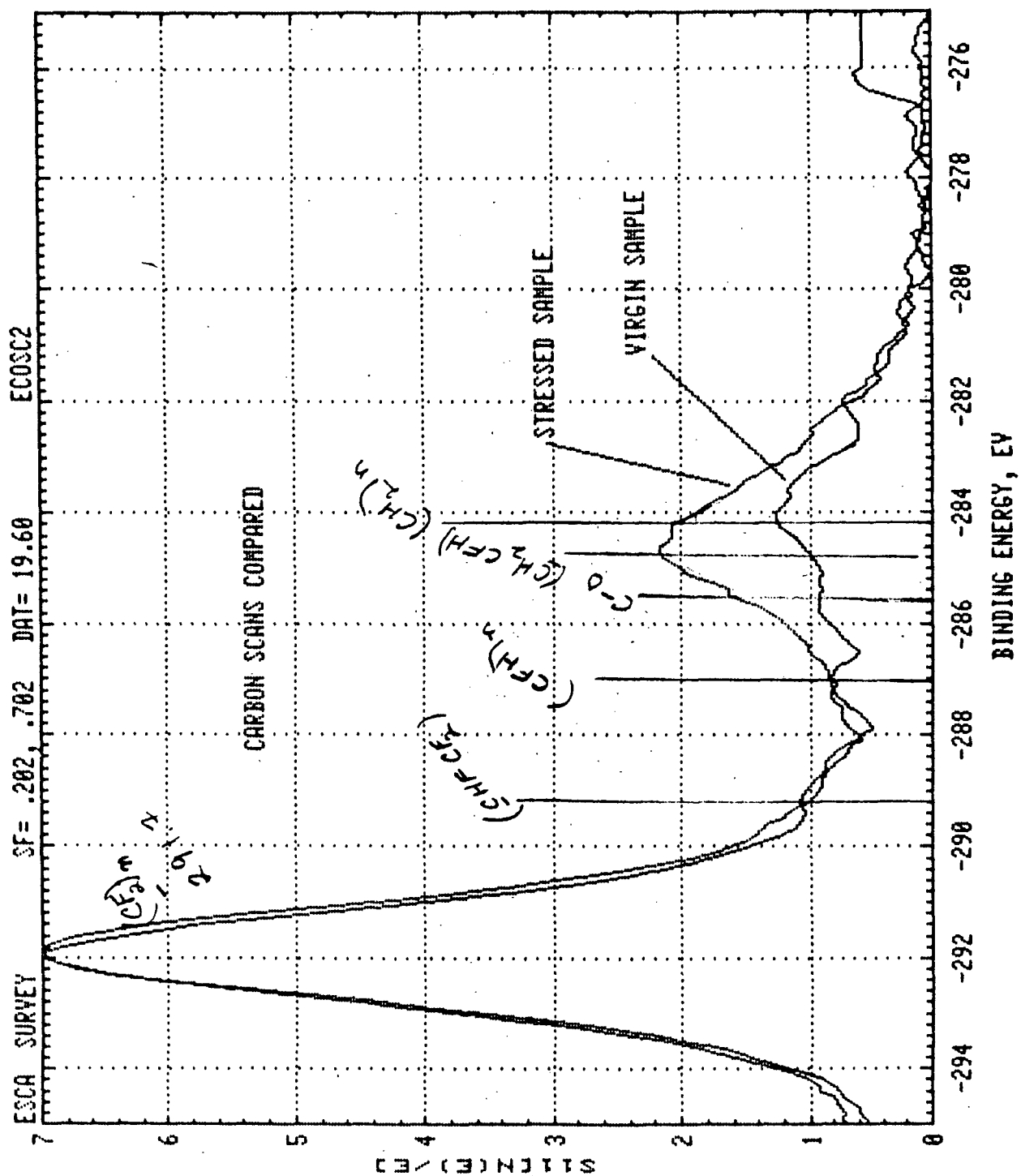


Figure 6.2: Oxygen Scan - ESCA

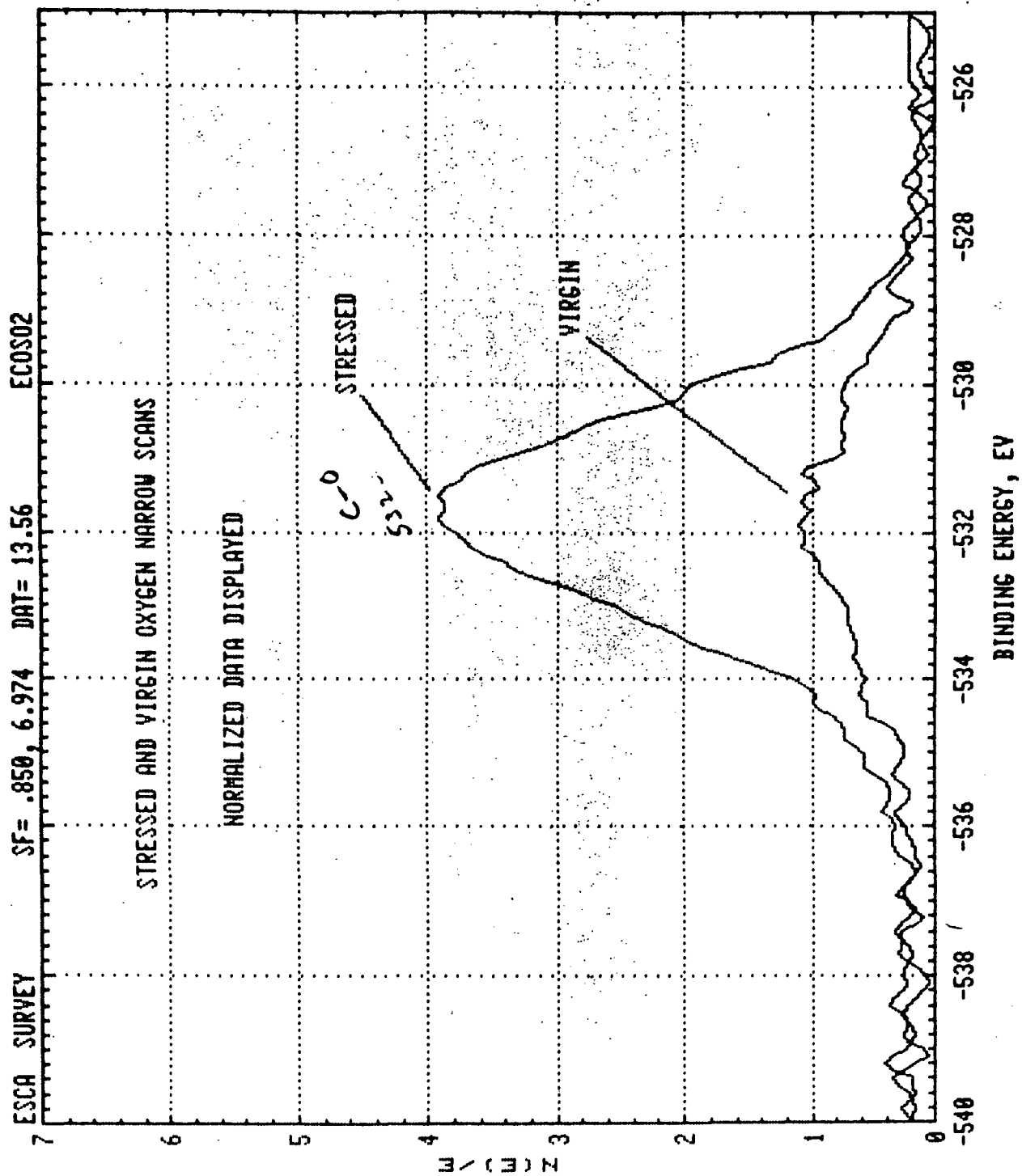
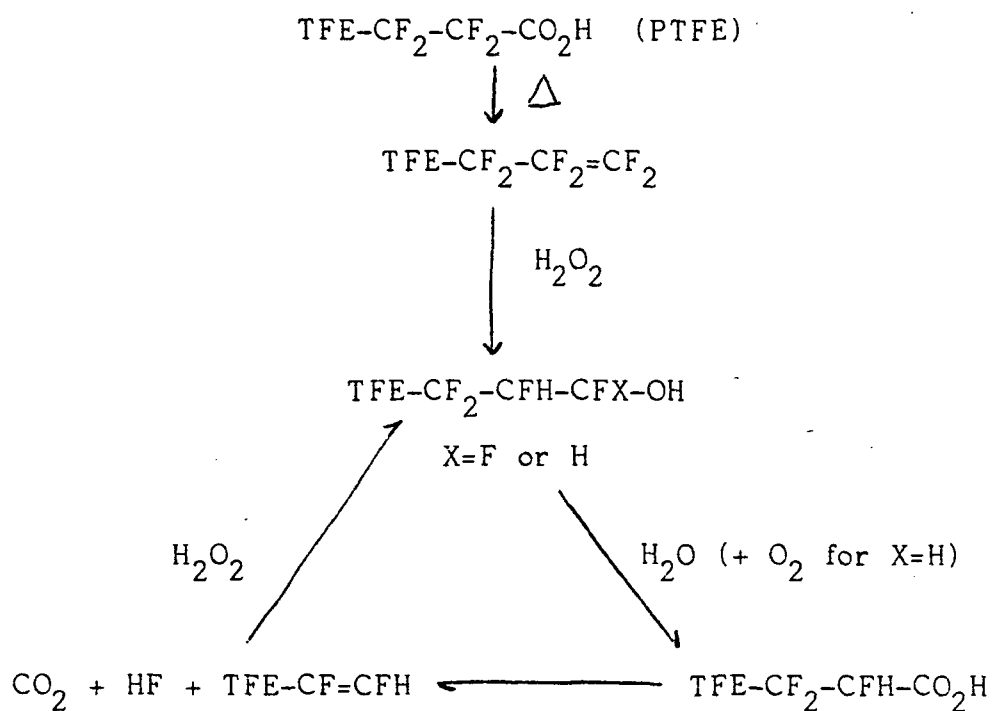


Table 6.4

¹⁴C-Specific Activity Change in
Cathodes Stressed in Half-Cells

<u>Cathode</u>	<u>Specific Activity, DPM/mg</u>		
	<u>before</u>	<u>after</u>	<u>change, %</u>
Pt #4	126.8	116.8	8
Pt #5	292.3	250.7	13

Figure 6.3 Degradation Mechanism for PTFE



stressed PTFE would be observed. The remaining PTFE should have increased CFH content as described in Section 6.2.4 based on ESCA evaluation.

6.4 Summary

PTFE has been shown to be unstable in the primary fuel cell environment, based on physical and chemical measurements. Surface wetting angle was observed to change significantly; surface chemistry was observed to change, based on ESCA measurements. The PTFE degradation mechanism proposed of degradation of carboxyl polymer chain end-groups was verified, based on change in specific activity of ^{14}C -labeled PTFE and on ESCA measurements.

7.0 Evaluation of Dimeric TAA

7.1 Introduction

The initial work done under the program showed TAA to be an active catalyst for the oxygen dissolution reaction; work by Collman et al., [*J. Electroanal. Chem.* 101:117 (1979)] and others suggested that when organometallic catalysts are held closely together through covalent bonds, less hydrogen peroxide is produced. Therefore, ECO attempted to evaluate the electrochemical performance of TAA which is held, via two carbon links, so that the planar TAA molecules are stacked parallel.

7.2 Pulse Voltammetry Evaluation

Pellets were prepared, catalyzed with either sintered bis-benzocyclobutene-CoTAA (dimeric-CoTAA; Product K) or bis-diazo-benzobutene-CoTAA (diazo-dimeric-CoTAA; Product L); they were evaluated by voltammetry following the procedure described in Section 4.3.2; the results obtained are provided in Table 7.1. Comparison of peak current density (mA/cm^2) observed for the dimeric TAAs with that observed for the controls (Vulcan, platinum oxide and sintered CoTAA) shows that the dimeric TAAs have improved performance. The diazo-dimeric CoTAA was observed to be the most active; this molecule should be held covalently both 'face-to-face' and linked to the carbon surface (via radical reaction induced by heating of the diazo group).

7.3 Half-Cell Cathode Evaluation

Wet-proof cathodes containing the dimeric TAAs were prepared and tested following the procedures described in Section 5.1.1. These cathodes were stressed in 100°C 85% phosphoric acid and IR-free performance data obtained; these data are shown in Table 7.2. These results are rather surprising in that cathodes catalyzed with dimeric CoTAAs were observed to have Tafel slopes approximately equal to platinum but significantly less than CoTAA.

Long-term half-cell tests were run (1000 hours) on cathodes catalyzed with diazo dimeric CoTAA; the results of this test showed that dimeric CoTAA has increased temperature stability compared to CoTAA: approximately equal performance decay was observed with a 25°C difference in electrolyte temperature (approximately 17 and 22% decay at 125° and 100°C respectively).

7.4 Summary

CoTAA, which was covalently linked to both the carbon surface and to form a planar lattice, was evaluated. This dimeric material appears to be more temperature stable and to have improved electrochemical activity (as measured by pulsed voltammetry) compared to CoTAA. The lack of improved catalytic

Table 7.1

Pulse Voltammetry Data on TAA-Catalyzed Pellets

<u>Carbon Type</u>	<u>Peak Current Density, mA/cm²</u>	
	<u>Temperature, °C</u>	
	27°	100°
Vulcan XC-72	8.8	31.3
Platinum oxide on Vulcan XC-72	46.3	115.8
2/1-sintered CoTAA on Vulcan XC-72	37.8	159.3
2/1-sintered Co butene-TAA on Vulcan XC-72	47.0	163.3
2/1-sintered Co bis-diazo-butene-TAA on Vulcan XC-72	62.8	187.3

Table 7.2
Performance of Various Cathodes
after 100 hours*

<u>Catalyst</u>	<u>Rest Potential in O₂ at 100°C (mV)</u>	<u>Tafel Slope at 100°C (mV/decade)</u>	<u>Potential at 10 mA/cm² (mV)</u>
Platinum	960	130	640
CoTAA	830	60	658
Dimeric CoTAA	813	180	540
Diazo Dimeric CoTAA	821	160	590

* Cathodes held at 100°C at 650 mV vs DHE during test period except for the diazo dimeric CoTAA which was held at 125°C.

performance observed in half-cell tests may be a function of the spacing between the CoTAA molecules in the lattice.

8.0 Electrode Fabrication Technique

8.1 Introduction

The level of performance of TAA-catalyzed cathodes in half-cells was used to rank the TAAs; all the cathodes were prepared by a uniform procedure which was identified early in the program. However, during the course of the program the value of this initial procedure in providing uniformly performing cathodes was questioned. Therefore, toward the end of the program, some time was spent developing a new method which would provide more uniform cathodes.

8.2 Long-Term Half-Cell Test

The initial fabrication procedure used was developed to provide thin catalyzed layers of more uniform performance. This procedure was based on using a support of stiff carbon fabric (PWB-35) from Stackpole Fibers, Inc. Two carbon layers were deposited in this fabric: first 50 mg of 30%/70% Teflon (DuPont Type 3416 washed with methanol)/Vulcan XC-72 was filtered through the 3.2 cm dia. circle of fabric in a Buchner funnel using 75 ml of Freon 113; then a second layer of 100 mg of 30%/70% Teflon/33% CoTAA sintered with bonded Vulcan XC-72-CoTAA was applied. The matrix was placed on a gold-plated expanded titanium screen and pressed at 320°C/1000 psi for 5 min. The resultant catalyst layer is 0.10 mm thick and contains approximately 3.9 mg cobalt. Initial performance of this electrode using sintered CoTAA as the catalyst in 100°C conc. phosphoric acid was 12.8 mA/cm² at 0.650 V vs H₂; performance was monitored until cathode failure occurred (297 days). The cause of failure was electrode flooding. As shown in Table 8.1, cathode performance had decayed approximately 30% over the test period.

8.3 Electrode Fabrication Technique for Improved Cathodes

8.3.1 Introduction

The use of an aqueous dispersion of PTFE to give fuel cell cathodes their hydrophobic character is the basis for the present day technology in the fabrication of fuel cell cathodes. The performance of these "Teflon bonded" platinum on carbon electrodes is limited by the size of the effective catalyst clusters, of agglomerates, interspersed between the gas diffusion channels maintained by the PTFE. When a conventional platinum on carbon electrocatalyst is combined with a wet proofing agent such as PTFE, the resulting mixture contains large aggregates of catalyst of varying dimensions mixed with a random admixture of PTFE. The fuel cell performance of cathodes made from this type of mixture is poor.

Techniques have been developed to overcome this problem. The basis for these techniques involves addition of chemical

Table 8.1

Long-Term Performance of a CoTAA-Catalyzed Cathode

<u>Time, days</u>	<u>Performance, mA/cm²*</u>
0	12.8
62	12.6
140	11.2
170	10.2
230	9.8
297	9.0

* Performance measured at + 0.650 V vs hydrogen in 100°C 85% phosphoric acid.

salts, acids, or bases to the mixture of aqueous PTFE and catalyst. In theory, the purpose for adding these substances is to control the colloidal interactions (ie: by adjusting the surface charges of the electrocatalyst and binder particles, the zeta potential of the suspended particles is altered, consequentially altering the diffusion layer of these particles and the interactions between them). This results in a more even dispersion of the PTFE on the surface of the electrocatalyst particles - the result is a flocculate of the two. The measure of success in evenly dispersing the PTFE on the electrocatalyst is the "floccing" of the two components. This is a qualitative parameter, and consists of viewing the supernatant after adding and mixing all of the components. If floccing is successful the supernatant will be clear; if unsuccessful, the supernatant will be clouded with the unflocced PTFE.

The qualitative approach to dispersing PTFE in the electrocatalyst is the main reason for the success in improving the performance of the platinum on the carbon cathode. Unfortunately, all of the flocculating techniques developed to date are for platinum on carbon catalysts. As a result, there is some question as to whether or not these techniques would successfully lend themselves to the ECO CoTAA electrocatalyst.

8.3.2 New Fabrication Technique

The procedure for preparing an aqueous dispersion of platinum or CoTAA on carbon electrodes consists of the following. A 15 mg/cm² total solids loading was the target, therefore 100 mg of catalyst was added to a 10 ml beaker. The ICI Teflon (AD1) dispersion has a density of 1.5 g/cc and is 60 % solids by weight: therefore 0.05 cc of AD1 was added to another 10 ml beaker. Ten ml of deionized water was added to each beaker and the two solutions were separately mixed using the ultrasonifier for 10 mins. The two solutions were then mixed together and the floccing agent of choice (ie: 1 ml 1x10⁻² M LaSO₄, adjusting pH with HNO₃ or bases) was added. The mixture was stirred and then rapidly filtered onto the support substrate (Stackpole Fiber). The electrode was then pressed at 500 psi several times between 2 pieces of filter paper to remove excess water. The electrode was then dried at 100°C for 2 hours to drive off the Triton X-100 surfactant present in the AD1. The dried electrode was then sintered at 320°C for 15 mins.

8.3.3 New Cathode Performance

One platinum electrode was prepared using Prototech 10% Pt on carbon employing the technique described in Section 8.3 with 1x10⁻² M LaSO₄ as the floccing agent. Table 8.2 provides a comparison of the performance of this electrode against the performance of an electrode made using the original Freon dispersion technique, and a Prototech RA2 electrode. It should be noted that LaSO₄ brought about floccing of the platinum catalyst

Table 8.2

Comparison of Performance of Platinum Catalyzed Cathodes*

<u>Cathode</u>	AD1 Floc	Freon Disp.	RA2
<u>Current Density</u> , mA/cm ²		<u>Potential</u> , mV vs DHE	
0.5	950	930	930
1	930	890	890
10	790	775	770
50	710	650	700
100	670	590	660

* IR-free performance in 125°C, 85% phosphoric acid using O₂ as fuel.

in the prescribed manner; these results indicate that we are capable of employing this technique to provide cathodes comparable to commercial cathodes.

Attempts to floc the C-3 CoTAA catalyst using the suggested floccing agents were not successful. However, after varying the pH adjustment technique, a measure of success was achieved. In future work a cathode will be prepared for testing using this floccing technique.

Appendix A: List of Products with Molecular Weight

<u>Product</u>	<u>Name</u>	<u>Mol. Weight</u>
A	TAA: dihydrodibenzo tetraazannulene ($C_{19}H_{17}N_4$)	301
B	Bis-aminated TAA: bis-(dimethyl-aminomethylene)-mono-(dihydrodibenzotetraazannulene) ($C_{25}H_{29}N_6$)	431
C	Acylated carbon: carbon functionalized to have an acyl link covalently bonded to its surface ($C_6H_{10}ClO$)	133.5
D	Cyclized carbon: carbon functionalized to a ring formed through covalent bonding of a pentyne (C_5H_5Cl)	100
E	Alkylated carbon: carbon functionalized to have an alkyl link covalently bonded to its surface using an aluminum trichloride catalyst ($C_6H_{12}Cl$)	119
F	Alkylated carbon: carbon functionalized to have an alkyl link covalently bonded to its surface using a potassium/naphthalene catalyst ($C_6H_{12}Cl$)	119
G	CoTAA bonded to carbon via an alkyl link: Product B reacted with Product E or F and then metallated with cobalt acetate	
H	Heat-sintered bonded CoTAA: Product G mixed 2:1 with sublimed cobalt TAA and then heated in an inert atmosphere for one hour at 800°C	
I	Bis-(phenyl diazo)-dibenzocyclobutene tetraazaannulene ($C_{32}H_{28}N_6$)	500
J	4,5-bis-aminobenzocyclobutene ($C_8H_6N_2$)	130
K	Cobalt bis-dibenzocyclobutene tetraazaannulene ($CoC_{22}H_{16}N_4$)	395
L	Cobalt bis-(phenyl diazo)-dibenzocyclobutene tetraazaannulene ($CoC_{32}H_{26}N_6$)	557

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16. Abstract Alkylation of Vulcan XC-72 has been shown to provide the most stable bond type for linking CoTAA to the surface of the carbon; this result is based on data obtained by cyclic voltammetry, pulse voltammetry and by release of ¹⁴ C from bonded CoTAA. Half-cell tests at 100°C in 85% phosphoric acid have shown that CoTAA bonded to the surface of carbon (Vulcan XC-72) via an alkylation procedure is a more active catalyst than is platinum based on a factor of two improvement in Tafel slope; dimeric CoTAA has catalytic activity equal to platinum. Half-cell tests also have shown that bonded CoTAA catalysts do not suffer a loss in potential when air is used as a fuel rather than oxygen. Commercially available PTFE has been shown to be unstable in the fuel cell environment with degradation occurring in 2000 hours or less. PTFE was stressed at 200°C in concentrated phosphoric acid as well as electrochemically stressed in 150°C concentrated phosphoric acid; the surface chemistry of PTFE was observed to change significantly as measured by goniometry and by an ESCA technique. Radiolabeled PTFE was prepared and used to verify that such chemical changes also occur in the primary fuel cell environment.					
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